THE SPECTROGRAPHIC ANALYSIS OF TIN AND TIN-LEAD SOLDERS

D. M. SMITH, A.R.C.S., B.Sc., D.I.C., F.Inst.P.

Spectrographic Department,
Research Laboratories, Johnson, Matthey & Co. Ltd.,
Wembley, Middlesex.

PAGE

Preface 3

GENERAL OBSERVATIONS ON SPECTROGRAPHIC METHODS

A. Choice of Spectrograph 4
Spectrograph slit irradiation 4
B. Plate Processing 5
C. Analytical Interpretation of Spectra 6
1. *Early methods* 6
2. *'Comparison Standard' method* 6
3. *'Internal Standard' method* 7
4. *The use of Auxiliary spectra* 7
5. *The Logarithmic Sector (Wedge) method* 8
6. *Densitometer (Microphotometer) technique* 8
7. *Photographic plate calibration* 9
D. Excitation Sources 12
1. *D.C. Graphite arc ('globule' technique)* 12
2. *Simple condensed spark* 12
3. *Intermittent A.C. arc* 13
4. *Multisource and General-Purpose Source Units* 14

ANALYSIS OF TIN

1. *Standard Alloys* 15
2. *Preparation of Samples for Analysis* 17
3. *The Spectra of Successive Exposures* 17
4. *Prespark Period* 18
5. *Standardised Spark Technique (B.N.F.M.R.A.)* ... 19
6. *Analytical Tables* 19
7. *Limits of Detection* 21
Appendix: Laboratory Purification of Tin by Electro-Refining ... 22

ANALYSIS OF TIN-LEAD SOLDERS

1. *Standard Alloys* 23
2. *Residue Method* 23
3. *Comparison of Synthetic Residues with Residues from Alloys to be used as Metallic Standards* 25
4. *Standardised Spark Techniques* 25
5. *Choice of Internal Standards* 26
6. *Analytical Tables:*
(*a*) *B.N.F.M.R.A.* 27
(*b*) *Fry's Metal Foundries Ltd.*... 28
7. *Effect of Antimony as a Third Alloy Component* ... 29
8. *A.S.T.M. Tentative Standard Method* 29

BIBLIOGRAPHY 30

820.
G·176.

Preface

EARLIER work on the spectrographic analysis of tin, carried out by the British Non-Ferrous Metals Research Association, dealt with the quantitative determination of small quantities of antimony, bismuth, cadmium, copper, lead and silver. The results of this work were published in Research Monograph No. 2, 'Metallurgical Analysis by the Spectrograph', by the author (1933).

Later, at the request of the International Tin Research and Development Council, the research on the spectrographic analysis of tin was extended with particular reference to the quantitative determination of small quantities (1 per cent and less) of aluminium, cadmium and zinc. This was published as I.T.R.D.C. Tech. Publ. A, No. 46, November, 1936.

A further investigation extended the work to the analysis of tin-lead solders for small amounts (of the order of 0·1 per cent and less) of aluminium, bismuth, cadmium, copper and zinc. In view of the difficulties in obtaining satisfactory chemical checks on the composition of the standard alloys, synthetic residues were prepared by mixing solutions of the various constituents in the appropriate proportions and evaporating to dryness.

This work was proceeding in 1939 but at that time it became impossible to continue the study of improvements in the technique for the spectrographic analysis of residues as had been contemplated.

An interim report describing the results obtained by that time, and giving suggestions for further study of the problems outstanding, was published as Tin Research Institute Publication No. 105, September, 1941.

All the above investigations were carried out in the laboratories of the British Non-Ferrous Metals Research Association with the aid of funds provided by the International Tin Research and Development Council.

Little further work appears to have been published in Great Britain, the most important advance in the analysis of tin being reported from the U.S. National Bureau of Standards, Washington, by B. F. Scribner.

This booklet aims at giving a summary of present knowledge, mostly published but in part unpublished, on the subject, together with such information on choice of equipment and suitable methods of analysis as will enable the reader to select the spectrographic technique most suitable for his analytical requirements. Spectrographic analysis has not yet reached a position that one can recommend a particular method as being unquestionably the best; the most that can be done is to indicate the methods that have proved successful in certain laboratories.

The author wishes to thank the Directors of Johnson, Matthey & Co. Ltd., for permission to include a reference to the method used in the Company's spectrographic laboratory for analysing high purity tin, and for other facilities. The author is also indebted to Mr. P. Courtney and Mr. R. J. Fay, spectrographer, both of Messrs. Fry's Metal Foundries Ltd., for co-operation with regard to chemical and spectrographic analysis.

GENERAL OBSERVATIONS ON SPECTROGRAPHIC METHODS

For a general introduction to the subject, those unacquainted with spectrographic analysis are recommended to consult the books by F. Twyman[29] and W. R. Brode[30].

A. Choice of Spectrograph

Since most of the persistent impurity lines are to be found in the ultraviolet region of the spectrum, spectrographs with quartz prisms and lenses are used, as quartz will transmit these radiations. Grating spectrographs are also used in the U.S.A. but have not yet been adopted in this country for metallurgical spectrography.

It is not proposed to discuss the proper setting up and alignment of the spectrograph as this is usually fully dealt with in the instructions supplied by the makers of the instrument. The optical bench type of mounting for the arc or spark stand, together with an optical gauge for setting the position and length of the discharge, is recommended for routine work on account of its rigid construction.

Except when analysing tin samples with high iron contents, a medium-size spectrograph should prove adequate, particularly the modern flat-field instrument. The tin spectrum is comparatively simple and the possibilities of coincidences, between impurity lines and lines of other impurities and of tin, are remote. This type of spectrograph has the advantage that the whole spectrum from the ultraviolet to the visible is photographed at once on a 10×4 in. plate (length of spectrum from 2,100 to 8,000 Å, about 19·6 cm.). With the Littrow spectrograph, giving about three times the dispersion, two or three settings will be required to cover the whole spectrum. This is a simple matter with the modern fully automatic instrument, but it increases the time taken by the analysis, unless all the useful lines appear in one restricted region.

Scribner[16] used a Littrow spectrograph as it gave reduced spectrum background and wider separation of the lines, both of which features are advantageous from the point of view of accurate photometric measurements.

Spectrograph Slit Irradiation

Various methods of irradiating the spectrograph slit have been used and the choice of method depends on the type of analytical work being done.

Method 1. In the early use of the graphite arc (globule) method the arc was focused on the slit by means of a spherical lens, giving an enlarged stigmatic image. A concave aluminised mirror can also be used and this has the advantage of achromatism (i.e. the image is in focus for all wavelengths). Light from the central part only is allowed to enter the spectrograph, radiation from the positive graphite pole and from the molten globule being excluded by means of a diaphragm just in front of the slit. This method is unsuitable for quantitative analysis by means of spark spectra on account of the 'pole' effects (as illustrated in Plate I).

Method 2. The method recommended for accurate quantitative analysis, with the densitometer, is to focus the discharge within the optical system of the spectrograph (i.e. on the collimator lens or on the prism face). This gives maximum uniformity of illumination along the length of the spectrum lines.

When using wedge or sector methods, this procedure is essential as a much longer slit is used than in other methods (5 mm. or more, as compared with 1 or 2 mm.).

Method 3. For trace analysis it is an advantage to use no intervening condensing lens and to place the source at a distance of 20 cm. from the spectrograph slit. Shorter times of exposure can be used than with method 2 and this is an advantage in the case of an easily oxidised metal like tin. This method can be used for both arc and spark spectra.

B. Plate Processing

Recommendations for the processing of photographic emulsions have been made by the Photographic Panel of the B.N.F.M.R.A.[28a] primarily with the object of securing maximum uniformity over the plate. The recommendations may be briefly summarised as follows:

Developer: Either Kodak D.19*b* (diluted 1 in 3) or Ilford I.D.2 are equally satisfactory.

Temperature of Development: Should be standardised at 68° F. (±1° F.).

Method of Development: Three methods are discussed, viz.:

(i) simple dish rocking;
(ii) using a multiple blade squeegee;
(iii) brushing.

Of the three methods, brushing gives the best results, and there seems to be no significant difference between simple dish rocking and the squeegee method. It is essential to ensure rapid removal of the products of development by adequate agitation of the developer. This requires the use of a large dish (at least 14 in. × 8 in. is recommended for a 10 in. × 4 in. plate) with some device for centring the plate and the avoidance of unidirectional flow of developer.

Time of Development: Should not be less than 4 minutes.

Rinsing: It is recommended that the plate be rinsed in water containing 2 per cent acetic acid, for 10 seconds.

Fixing: A hardener fixing bath is recommended.

Washing: Between 15 minutes and 2 hours in running water. If the water is hard, a final rinse in distilled water is recommended.

Drying: Surplus moisture should be removed by wiping the plate with a soft damped chamois leather or viscose sponge. The plate should then be dried in a gentle current of air at room temperature.

The plates generally recommended for spectrographic work are: Ilford Ordinary and Thin Film Half-Tone, Kodak B.10 and B.20; although Ilford Special Lantern plates have been used with satisfactory results. If an examination of the visible region is required (e.g. for the detection of the alkali metals) Ilford Long Range Spectrum plates are recommended, as these plates are sensitive to about 8500 Å.

C. Analytical Interpretation of Spectra

All methods of quantitative spectrographic analysis are based on the fact that in the arc or spark spectrum of a metal or alloy, impurity lines or lines due to alloying elements increase in intensity as the percentage of each element in the alloy increases. The first lines to appear, when only traces of impurities are present, are the most persistent lines (often still referred to in the literature as *raies ultimes*) and these are the lines first sought in qualitative analysis. Such lines are characteristic of the elements as they always appear in the same positions in the spectrum, i.e. they are of definite known wavelengths. As the percentage content increases these lines increase in intensity and further lines begin to appear.

When the spectra are photographed, as is the usual practice,* the increase in intensity of these lines results in an increase in their density on the photographic plate, while the lines due to the basis metal appear with constant density. The problem of quantitative spectrographic analysis is consequently the correlation of the densities of the lines with the amounts of the elements present which give rise to them.

Various methods of analysis have been devised and these are briefly reviewed below:

1. Early Methods

The earliest attempts at quantitative analysis were based on the number of impurity lines present. This method has obvious limitations and is only approximately semi-quantitative.

2. 'Comparison Sample' or 'Comparison Standard' Method

In this method direct comparison is made between the spectra of the samples under test and those of a range of standard alloys of known analysis. All the spectra are photographed on the same plate, using standardised electrical and optical conditions for both samples and standards.

The analysis may then be made by visual comparison or by photometric measurements of the densities of the lines in the different spectra. Kringstad[7] used the former method for the determination of lead in commercial tin and he gives a table showing satisfactory agreement between spectrographic and chemical analyses. Meggers, Kiess and Stimson[1] used a photometric method in which intensities were matched with the brightness of an electrically heated tungsten wire, and applied it to the analysis of fusible tin plugs for copper, lead, iron, zinc, nickel, silver, and bismuth.

In present-day applications of the densitometer† use is made of the 'internal standard' principle as a means of compensation for slight fluctuations in the density of the spectra.

* Successful use has recently been made in America of the photomultiplier tube for direct recording of spectral line intensities—see G. H. Dieke and H. M. Crosswhite, *J.Opt.Soc.Amer.*, 1945, **35**, (7), 471-480, and subsequent publications in that journal. These methods have not so far been developed in this country.

† The use of the term 'Densitometer', in place of the more customary 'Microphotometer', is recommended by the Spectrographic Discussion Group, Glasgow (Publication No. 1: *Suggested Definitions of Terms used in Spectrographic Analysis* 1946). The recommendations of this group have been followed in this publication.

3. 'Internal Standard' Method

Many attempts have been made to devise 'absolute' methods of analysis, i.e. methods which do not require the use of standard alloys for comparison once the preliminary standardisation of the method has been carried out. While none of these methods has proved entirely successful in this respect, the first method, the 'internal standard' method, devised by W. Gerlach* forms the basis of practically all the methods in use today. In this method the intensities of the analysis lines are compared with those of neighbouring lines due to the predominant metal in the alloy, or the basis metal in the case of the determination of impurities.

Analytical tables compiled from such data have been extensively used for rapid visual estimations of impurity contents, and examples are given in the present publication (see Tables III–XI for the analysis of tin and Tables XVII–XXI for the analysis of solders).

Pairs of lines are chosen, wherever possible, the relative intensities of which are largely independent of variations in the electrical conditions of excitation of the spectra. Such pairs are referred to as 'homologous pairs'.† Scheibe, Linström and Schnettler[4] emphasise that arc lines must be compared with arc lines and spark with spark, in the selection of homologous pairs for analysis by the internal standard method.

4. The Use of Auxiliary Spectra

In cases where there are few suitable lines available as intensity standards in the neighbourhood of the analysis lines, the number of such standards may be artificially increased by the use of an auxiliary spectrum which is coupled with that of the sample under test. The coupling is effected by varying the time of exposure until a selected pair of lines, one in each spectrum, are of equal intensity. (The spectra are photographed either superimposed, or preferably overlapping, in order that the additional lines may be easily recognized.) This auxiliary spectrum principle was first applied to the analysis of metals and alloys by Gerlach.‡

The method of using an auxiliary alloy as a standard comparison sample, as developed in the B.N.F.M.R.A. Laboratory, has certain advantages over the use of a coupled under-exposed spectrum of a different metal from the one being analysed. The lines due to the added component in the alloy are intrinsically of the same nature as the impurity lines in the spectra of the samples under test, and therefore more suitable for comparison. For ease in comparison the two spectra are photographed in juxtaposition.

Thus for the analysis of tin, the use of an auxiliary alloy of tin, with a small quantity of an element giving lines of suitably graded intensities for use as addition intensity standards, would increase the number of line pairs available for comparison, thereby enabling closer percentage intervals to be determined. While this has not been tried for the analysis of tin, it is the author's experience in the case of the routine spectrographic analysis of lead[28], that the results of different observers agree more closely when using the auxiliary alloy method than when the internal standard method alone is used.

* *Z. anorg. Chem.*, 1925, **142**, (3–4), 383.

† E. Schweitzer. *Z. anorg. Chem.*, 1927, **164**, 127–144.

‡ *Z. Metallkunde*, 1928, **20**, 248–251.

5. The Logarithmic Sector (Wedge) Method

The logarithmic sector principle was first devised by L. Hamburger and G. Holst* as a method of measuring relative line intensities in multiplets. It was first applied to analytical work by Scheibe and Neuhäusser[8], who, in a paper mainly concerned with alloying components in iron, gave results for the determination of 0·1 to 3 per cent lead in tin.

The sector, which is in the form of a metal disc, the periphery of which is shaped in the form of a logarithmic spiral (or the disc may have a logarithmically cut aperture) is rotated just in front of the spectrograph slit. This varies the effective time of exposure along the length of the slit, so that the spectrum lines decrease in intensity along their length and finally disappear. Wedge shaped lines are thus obtained in the spectrum, the length of a line being proportional to the logarithm of its intensity, or

$$\log \frac{I_2}{I_1} = K(l_2 - l_1)$$

where I_2 is the intensity of the impurity line and I_1 that of the internal standard, the corresponding lengths of the lines being l_2 and l_1.

The difference between the lengths of the lines forming a homologous pair is then correlated with percentage content.

Hitchen[10] used the method for the determination of arsenic, antimony, bismuth, copper, iron, lead, and zinc in tin, by means of both arc and spark methods. This work was followed later by Stewart[11], who did not use a densitometer as he considered that the sensitivity of this method was inadequate for the measurement of faint lines.

The principal objection to the method is the practical difficulty in determining the exact end-points of the lines, and the accuracy of analysis is of the same order as that of previous methods of visual comparison of line intensities. At the time this method was proposed, however, it represented a distinct advance, in that it was possible to obtain numerical data, and thus derive an average value of several determinations.

Various means have been proposed to overcome the difficulties in measuring the lengths of the lines, but the method remains subject to personal errors of visual estimation and is now rarely used.

6. Densitometer (Microphotometer) Technique

The direct reading densitometer (or microphotometer as it is generally referred to in this country†) is now a standard unit of spectrographic equipment and instructions for use are issued by the makers of the instrument. It is essentially an optical device whereby the densities of the lines used in quantitative analysis are measured as a function of the light transmitted by them and allowed to fall on a photoelectric cell. A magnified image (×10) is projected on to the densitometer slit, the width of which should be slightly less than that of the line image. The galvanometer should be shunted with a suitable resistance to give critical damping and a sensitivity control should be included so that the deflection for an unexposed portion of the plate ('clear plate' deflection) may be maintained at a constant value (usually 500 mm.).

* *Z. wiss. Phot.*, 1918, **17**, 265.

† See footnote on p. 6.

Then, provided that the galvanometer and photocell give a linear response to the light incident on the densitometer slit, the density is given by

$$D = \log_{10}\left(\frac{\text{deflection for clear plate}}{\text{deflection for line measured}}\right) = \log_{10}\frac{d_0}{d}$$

In practice, the density difference of a line pair is correlated with the logarithm of the percentage content. If the densities of the lines lie on the straight line portion of the characteristic curve of the photographic plate, the concentration-calibration curve (working curve) will be linear and of the form:

$$D_2 - D_1 = \log\frac{d_1}{d_2} = n\gamma \log C + \text{constant.}$$

where d_1 and d_2 are the densitometer readings (galvanometer deflections) for the internal standard and analysis lines, respectively
n is known as the emission factor
γ is the maximum slope of the characteristic curve
and C is the concentration of the element.

A further treatment of the subject, giving the derivation of this equation and its theoretical basis, will be found in Ref. 28(*b*), in which references to original contributions are quoted.

The concentration-calibration curve is constructed from density measurements on the line pairs in the spectra of standard alloys, photographed on the same plate as the samples for analysis.

Corrections for Variable Conditions

Many attempts have been made to apply corrections to the results of density measurements in the hope of increasing the accuracy of individual analytical determinations. Some of these are based on empirically found relationships, the chief virtue of which methods appears to lie in the fact that they are workable. At best, however, the compensation is only partial and by improving the excitation source (increasing its reproducibility) the fluctuations can usually be reduced to a point below the effectiveness of such corrections.

To compensate for the blackening properties of the photographic plate, standard methods of plate calibration are available, and these are discussed below.

7. Photographic Plate Calibration

It is generally accepted as the basis of quantitative spectrographic analysis that the ratio of the intensities of emission of two lines, one due to the impurity or alloying component being determined (analysis line) and the other due to the basis metal (internal standard) can be used as a quantitative indication of the amount of the element present. Since this ratio generally varies somewhat with the time of running the arc or spark discharge, standardised analytical procedures are determined by the condition that, over a specified interval of time, the combined effect of intensity and time of emission on the photographic plate shall be a reproducible quantity.

The use of standard alloy spectra for comparison automatically calibrates the photographic plate, but it suffers from the practical disadvantages of the time and material consumed each time an analysis is made.

The principal function of plate calibration is to enable the photographic plate to be used as a means of determining intensity ratios without making any assumptions as to the blackening properties of the plate itself. Various methods have been proposed, the principal types of which employ the following devices:

(*a*) Stepped Optical Wedge.

(*b*) Rotating Stepped Sector.

(The stepped spectra may be either of the sample under test or of an additional source of light.)

(*c*) Line Groups of known or pre-determined relative intensities.

(*d*) Constant Source.

(a) Stepped Optical Wedge

Preliminary results of the application of a stepped wedge or filter (made by depositing platinum in steps of increasing opacity on fused silica) to the determination of 0·02 to 0·6 per cent of lead in tin, are described by Follett[12]. The wedge is fixed in front of the spectrograph slit and the spectra obtained are in steps of different density corresponding to the optical densities of the steps of the wedge. A formula for the derivation of the intensity ratio of a line pair, from the densitometer readings on the lines and the known densities of the wedge steps is given by Follett. Since the absorbing medium is seldom optically neutral, it is necessary to calibrate the wedge at each wavelength to be used. The wedges are also fragile and for these reasons they have not been used for routine analyses to the same extent as the rotating stepped sector.

(b) Rotating Stepped Sector

A stepped disc, in which the angular apertures subtended by each step decrease with a constant ratio, is rotated just in front of the spectrograph slit, giving stepped spectra similar in appearance to those obtained with the stepped wedge. (Plate II shows a portion of the spark spectrum of a sample of commercial tin, obtained with a 7 step-sector.) This provides a time-scale method of calibration, but above a certain speed of rotation (the 'fusion frequency') it may be regarded as equivalent to an intensity-scale calibration. Blackening curves are plotted from density measurements on the stepped spectra and the quantity used in the construction of the concentration-calibration curve is the logarithm of the ratio of the times of exposure producing equal densities of the lines of the line pair selected. This is most accurately done graphically, by measuring the separation of the blackening curves along the log-exposure time axis. (Graphical calculators have been devised for the rapid computation of this quantity from the line densities in selected steps in the spectra.)

An account of the application of this method is given by Brackpot* who used it for the analysis of tin by means of arc spectra. [13, 14] Stroboscopic effects are a possible source of error in the case of intermittent sources such as the spark, but their occurrence does not appear to be frequent provided that the speed of rotation is suitably chosen.

A 5-step sector, rotated at 1,700 r.p.m., was used by Scribner[16], who constructed the plate calibration curve from densitometer readings on the tin line 2761·776 Å in the five steps.

* *Spectrochim. Acta* 1939, **1**, (2), 137–163. (A shorter account is given in *J. Inst. Metals*, 1939, **64**, 379–416.)

Correction for Spectrum Background. The necessity for background correction arises in determining the relative intensities of faint lines superposed on a spectrum background of comparable density, since the densitometer records the combined effect of line plus background. Methods of applying a correction are discussed in the following papers:

W. C. Pierce and N. H. Nachtrieb: *Ind. and Eng. Chem.* (*Anal. Edn.*), 1941, **13**, (11), 774–781.

R. O. Scott: *J. Soc. Chem. Ind.*, 1944, **63**, (1), 25–29.

R. L. Mitchell, R. O. Scott and V. C. Farmer: *Nature*, Feb. 16, 1946, **157**, 193–194.

No correction was made by Scribner[16] in the case of the arsenic line 2860·452 Å which was measured against the background associated with the strong tin line, 2863·327 Å, because of the uncertainty involved. Instead, one or two standards were exposed on the same plate and direct comparison of density differences was made.

(c) Line Groups

G. H. Dieke and H. M. Crosswhite* selected, for the purpose of plate calibration, groups of iron lines the relative intensities of which were found to be independent of the excitation conditions, and claim that this method gave satisfactory results. For the analysis of tin, this would require the photography of an iron spectrum on the same plate as the spectra of the samples under test. The calibration curve would then be constructed from density measurements on the selected iron lines.

(d) Constant Source

A series of exposures, of varied duration, of a constant source of light (e.g. a mercury vapour lamp) provides a time-scale calibration of the plate. This is undesirable as the correlation of intensity ratios with percentage content requires an intensity-scale calibration to be strictly valid. Moreover the constant source method requires several exposures (one for each point on the curve) as compared with the single exposure which suffices for the methods described above. For these reasons the method is not recommended.

Statistical Test of Reproducibility

Before using a spectrographic method for routine analyses it is desirable to carry out a statistical test of reproducibility.[28c] The standard deviation, which provides the most concise statement of the errors to be encountered, both as regards frequency and magnitude, is computed from the results of a large number of determinations (e.g. 50) on the same sample. It is calculated from the formula $\sigma = \pm\sqrt{\frac{\Sigma d^2}{n-1}}$ where d is the deviation of an individual result from the mean value and n is the number of determinations.

Scribner[16] obtained values of σ varying from 1·09 per cent (of the amount present) for copper to 2·52 per cent for iron, which represents a high degree of reproducibility.

* *J. Opt. Soc. Amer.*, 1943, **33**, (8), 425–434.

D. Excitation Sources

1. Direct Current Graphite Arc ('Globule' technique)

In earlier studies (prior to 1933) both the arc between metal electrodes and the globule arc technique were tried for the estimation of antimony, bismuth, cadmium, copper, lead and silver in tin. The arc between metal electrodes was abandoned as a routine method owing to its unsteady nature and the tendency for the electrodes to melt, even with low values of the current.

The following electrical and optical conditions were therefore standardised. A small pellet of the metal (0·1 to 0·2 gm.) was placed in a shallow cavity in the lower graphite electrode and a pointed graphite rod was used as the upper electrode. The arc was then struck between the graphite and the tin sample, the current being 1·5 amps. After the tin had melted into a globule and when the discharge had become steady (after about 5 secs.) the exposure was made. Short exposure times were found to be desirable as the metal rapidly becomes converted to oxide and the arc tends to run to the lower graphite electrode. The arc was focused on the slit of the spectrograph by means of a spherical condensing lens.

It was found that when the tin sample was made the negative electrode the spectra obtained under these conditions closely resembled those of the arc between metallic electrodes, the cyanogen band at 3883·4 Å (due to the graphite) being only faintly present.

In the application of this method to the determination of aluminium and zinc, however, irregularities in the spectra were observed. Even for small quantities of these elements no satisfactory correlation was obtained between percentage content and the intensities of the sensitive lines. It is possible that oxidation and selective volatilisation of these elements may have caused this.

Hitchen[10] used a globule arc, but made the sample the positive electrode and used a current of 3 amps. In order to keep the metal in a reduced condition he directed a small luminous gas flame on to the surface of the molten metal. (Some practice is required to make the flame cover the metal without being strong enough to extinguish the arc.)

Hitchen regards the spark as more satisfactory than the arc for the analysis of tin (a view which appears to be generally held), the arc method being unsuitable for the determination of arsenic and antimony.

Breckpot used a D.C. graphite arc method for the analysis of tin oxide[13] and found greater sensitivity when the sample was placed on the negative electrode. For the analysis of tin, either an arc between sufficiently massive electrodes[14] or between metal cathode and graphite anode was used[15], the arc length being 2 mm. and the current strength 1·2 amps. The determination of lead is quoted by way of illustration.

2. Simple Condensed Spark

The method of spark excitation most commonly used in this country is that given by a simple condensed spark circuit consisting of a $\frac{1}{4}$ KVA high reactance transformer, with secondary tappings to give 8,000–15,000 volts on open circuit. Capacity values range from 0·003 to 0·006 μF, the usual

value being 0·005 μF and a small value of added self-inductance is placed in series with the spark gap. This gives an 'uncontrolled' discharge. The usual procedure is to use two electrodes of the sample under test. Seith and Hofer[6], however, used a spark between the sample and a gold wire 2 mm. in diameter, a method also adopted by Kringstad[7].

In the earlier standardisation of spark spectra, the electrical conditions (either capacity or inductance, or both) were varied until equality of intensity was obtained between two selected lines of the basis metal, one an arc line and the other a spark line. Thus Gerlach and Schweitzer[3] used the arc line 3330·594 Å and the spark line 3352·435 Å in tin spectra. ('Fixation' pair.) In the spectrum reproduced in Plate I(*d*) this pair shows equality of intensity.

Since that time, however, difficulties have been experienced in attempting to reproduce a given set of conditions in a different laboratory from that in which they were originally standardised. This is attributed to the effect of leakage reactance of the transformer of the type used in this country, a factor which is seldom specified. Moreover, many effects previously attributed to inductance have now been shown to be due to its associated resistance.

This has been particularly evident in the case of the analysis of aluminium alloys where accurate analyses are required. While it is probable that this would not be of so much consequence in the determination of traces of impurities in pure metals, by visual methods of estimation, it would be as well to bear the possibility in mind in the case of the analysis of tin and tin-lead solders. The effect of a different set of excitation conditions would be to give different percentages of equality of intensity of lines forming pairs which are not strictly homologous.

Scribner[16] first used both 'uncontrolled' and controlled spark discharges, i.e. the simple spark circuit and a spark circuit with a synchronous interrupter, respectively. Both gave satisfactory results, but it was found that while a steady discharge was obtained with a 1 KVA, 15,000 V transformer (primary current 2·5 to 2·55 amps., capacity 0.003 μF and inductance 0·019 mH) an exposure time of 2 mins. was required to give spectra of suitable density. He therefore adopted a $\frac{2}{3}$ KVA, 35,000 V transformer, with 0·009 μF capacity, 0·335 mH added self-inductance and a synchronous interrupter. The spark gap was 4 mm.

3. The Intermittent A.C. Arc

An intermittent A.C. arc, in which a low-voltage discharge from a condenser is initiated (or 'triggered') by means of a low-energy high-frequency spark occurring at the voltage peak of the A.C. wave, has been successfully used for the determination of impurities in high purity zinc[24]. The circuit is a modification of the one devised by K. Pfeilsticker.* This source provides a higher degree of accuracy and the same order of sensitivity as given by the simple D.C. arc.

For these reasons, an intermittent A.C. arc, taking 5 amps., between pure graphite electrodes (globule technique) has been adopted in the Johnson, Matthey & Co. spectrographic laboratory for the analysis of high purity tin rods. Tests on a number of batches of this material have shown that this type of arc is well suited to the purpose.

* *Z. Elektrochem.*, 1937, **43**, (8), 719–721.

4. Multisource and General-Purpose Source Units

The modern trend in designing excitation sources is to provide for a wide variety of conditions of excitation, ranging from the arc to the spark, intermediate conditions being obtained by high-frequency triggering of low-voltage A.C. arc discharges. Recent examples of this type of source are given by the General-Purpose Source Unit of Walsh[25] and the Multisource Unit of Hasler and Dietert[26]. Both units are similar in principle, but the electrical details of the two circuits are different, particularly as regards the method of triggering, which affects the nature of the subsequent discharge. Other units, based on the same principle, again using different types of triggering have been constructed in this country but full details have not yet been published.* A similar type of variable source, known as the 'Emitator', has been constructed in Sweden[27]. This source is in the form of two units, one for high voltage and the other for low voltage.

So far as the author is aware, these excitation sources have not yet been applied to the analysis of tin or tin-lead solders.

* A source unit in which the discharge is initiated by means of 'Trigatron' gaps is described by C. Braudo and H. R. Clayton (*J. Soc. Chem. Ind.*, 1947, **66**, (8), 259-267). Results of reproducibility tests in the analysis of aluminium, using the controlled low voltage A.C. arc, are given.

ANALYSIS OF TIN

1. Standard Alloys for the Determination of Aluminium, Cadmium, Zinc, Silver and Antimony

(a) Alloys with Aluminium. (AL series: *prepared by the International Tin Research and Development Council.*)

All the alloys were made under a high flash point oil and cast, using a small Durville casting machine, into cast-iron moulds; 2·5 gm. of aluminium (weighed to an accuracy of 1 mg.) were added to 247·5 gm. of pure tin (accuracy of 0·05 gm.) and melted under oil at a temperature of approximately 450° C. The alloy was carefully stirred and cast, the ingot being marked AL1000 and containing 1·0 per cent of aluminium. The remainder of the alloys were then prepared by dilution of this alloy and cast at approximately 300° C.

Chemical analysis of the standard alloy AL1000 gave 0·996 per cent of aluminium. For the remainder of the series of alloys, experience has shown that under carefully controlled conditions of preparation, it is safer to rely on the synthetic figure than on chemical analysis where such small quantities are concerned. No attempts, therefore, were made to check these figures chemically.

(b) Alloys with Silver, Cadmium and Antimony added together. (TSCA series: *prepared in the B.N.F.M.R.A. Laboratory.*)

These standards were prepared by dilution of a temper alloy containing 0·5 per cent of each constituent, with Chempur tin, using the method of melting and casting in evacuated Pyrex tubes.

(c) Alloys with Zinc. (*i*). (ZN series: *prepared by the International Tin Research and Development Council.*)

The procedure was similar to that for the preparation of the aluminium standards. The zinc (weighed to an accuracy of 1 mg.) was added to pure tin, under oil, at approximately 400° C.

(*ii*). (TZ series: *prepared in the B.N.F.M.R.A. Laboratory.*)

Two alloys, with 1·0 and 0·1 per cent of zinc respectively, were prepared by melting and casting *in vacuo*, as a check on the composition of the corresponding ZN1000 and ZN100 alloys. In view of the difficulty of the chemical determination of small quantities of zinc in tin, the spectrographic check was accepted as being more certain.

(d) Alloys with Aluminium, Cadmium and Zinc, added together. (TACZ series: *prepared in the B.N.F.M.R.A. Laboratory.*)

In order to provide intermediate standards and as an additional check on the composition of the above alloys, a further series of alloys was prepared by dilution of a temper alloy (marked TACZ 10) containing 1 per cent of each of aluminium, cadmium and zinc, added together, with Chempur tin. The melting and casting were carried out *in vacuo*, as before.

Some difficulty was experienced in dissolving the aluminium. The tin was kept molten and agitated continuously for about 2½ hours in the hope of ensuring complete dissolution of the aluminium. Chemical analysis of this temper alloy, however, gave the following values of the aluminium content

(as determined on three separate portions): 0·7, 0·96 and 1·6 per cent respectively, thus showing an irregular distribution in the alloy.

Only those alloys whose aluminium contents were confirmed by comparison* with the standards supplied by the International Tin Research and Development Council were therefore adopted as intermediate standards. The aluminium content of the alloy TACZ 03 was found by chemical analysis to contain 0·026 per cent of aluminium. Alloys TACZ 004 and TACZ 003 were prepared by dilution of this alloy, and accordingly contained 0·0035 and 0·0026 per cent of aluminium, respectively.

(e) Alloys with Lead and Bismuth. (TLB series: *prepared in the B.N.F.-M.R.A. Laboratory.*)

These standards were prepared from electrolytically refined tin (see Appendix) by dilution of a temper alloy containing 0·5 per cent of each constituent, the melting and casting being carried out *in vacuo.*

The analyses of all the above synthetic alloys which were adopted as standards are given in Tables I and II.

TABLE I.—STANDARD ALLOYS WITH ALUMINIUM, CADMIUM AND ZINC

Mark	Al%	Mark	Zn%	Mark	Al%	Cd%, Zn%
AL1000	1·0	ZN1000 TZ10	1·0	TACZ10	—	1·0
AL100	0·1	ZN100 TZ1	0·1	TACZ07	—	0·07
AL50	0·05	ZN50	0·05	TACZ03	0·026	0·03
AL10	0·01	ZN10	0·01	TACZ009	—	0·009
				TACZ007	—	0·007
AL5	0·005	ZN5	0·005	TACZ004	0·0035	0·004
				TACZ003	0·0026	0·003
AL1	0·001	ZN1	0·001			

TABLE II.—STANDARD ALLOYS WITH SILVER, CADMIUM, ANTIMONY, LEAD AND BISMUTH

Mark	Ag%	Cd%	Sb%	Mark	Pb%	Bi%
TSCA5	0·5	0·5	0·5	TLB5	0·5	0·5
TSCA1	0·1	0·1	0·103	TLB1	0·1	0·1
TSCA05	0·005	0·005	0·053	TLB05	0·053	0·05
TSCA01	0·01	0·01	0·013	TLB01	0·013	0·01
TSCA005	0·005	0·005	0·008	TLB005	0·0076	0·0054
TSCA001	0·001	0·001	—	TLB001	0·0036	0·0014

Note: The compositions of the alloys containing the lowest amounts of added elements have been corrected by the amounts found chemically in the pure tin samples used.

* A 'synthetic spectrum' method, in which the spectra of a range of alloys were simulated by the superposition of the spectrum of the alloy with the highest content of the range on that of pure tin, the times of exposure being systematically varied, was used as a spectrographic check on the composition of the standards. The total exposure time (i.e. of standard alloy plus pure tin) was kept constant. While this method served a purpose at the time it was used (no densitometer being then available) it is no longer recommended, for both theoretical and practical reasons.

PLATE I

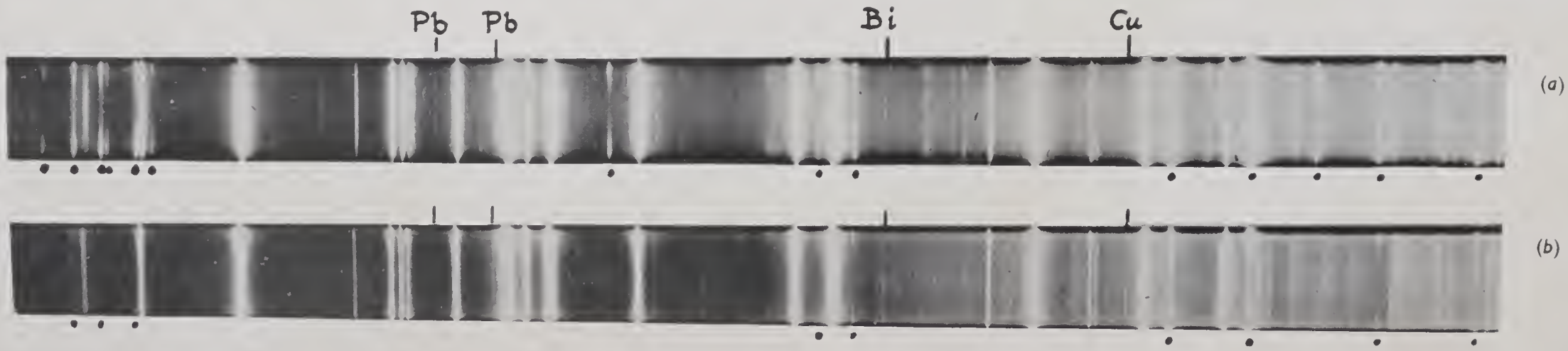
SPARK AND INTERMITTENT A.C. ARC SPECTRA OF PURE TIN

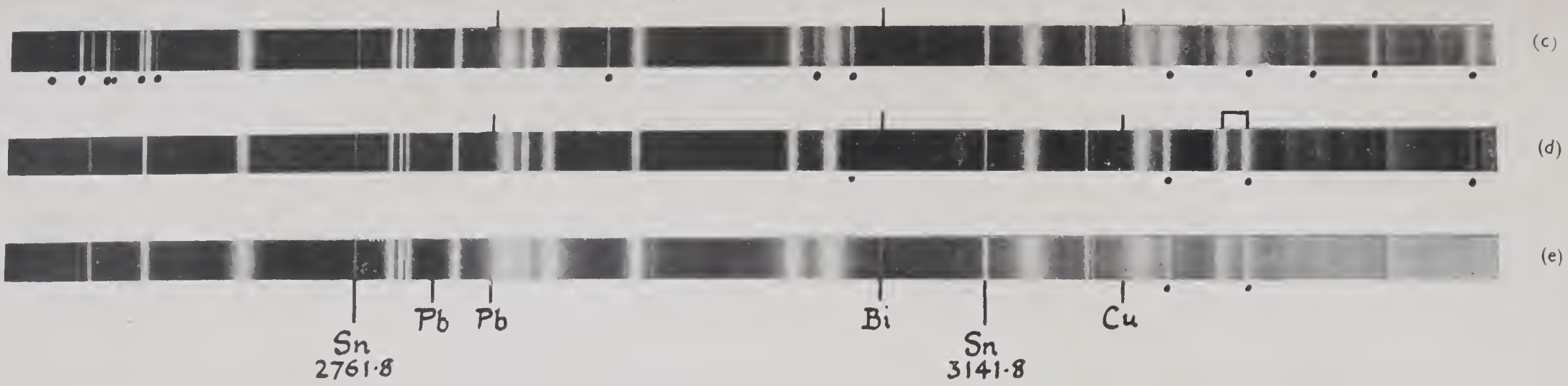
(*a*) Spark between metal electrodes, 0.03 mH added self-inductance.

(*b*) Spark between metal electrodes, 0.19 mH inductance. For both (*a*) and (*b*) the spark was focused on the spectrograph slit by means of a concave mirror.

(*c*) and (*d*) are the same as (*a*) and (*b*) respectively, but for these spectra the spark was placed 20 cm. from the spectrograph slit with no intervening condensing lens.

(*e*) Intermittent A.C. (globule) arc, taking 5 amps., between pure graphite electrodes. Slit irradiation as for (*c*) and (*d*).

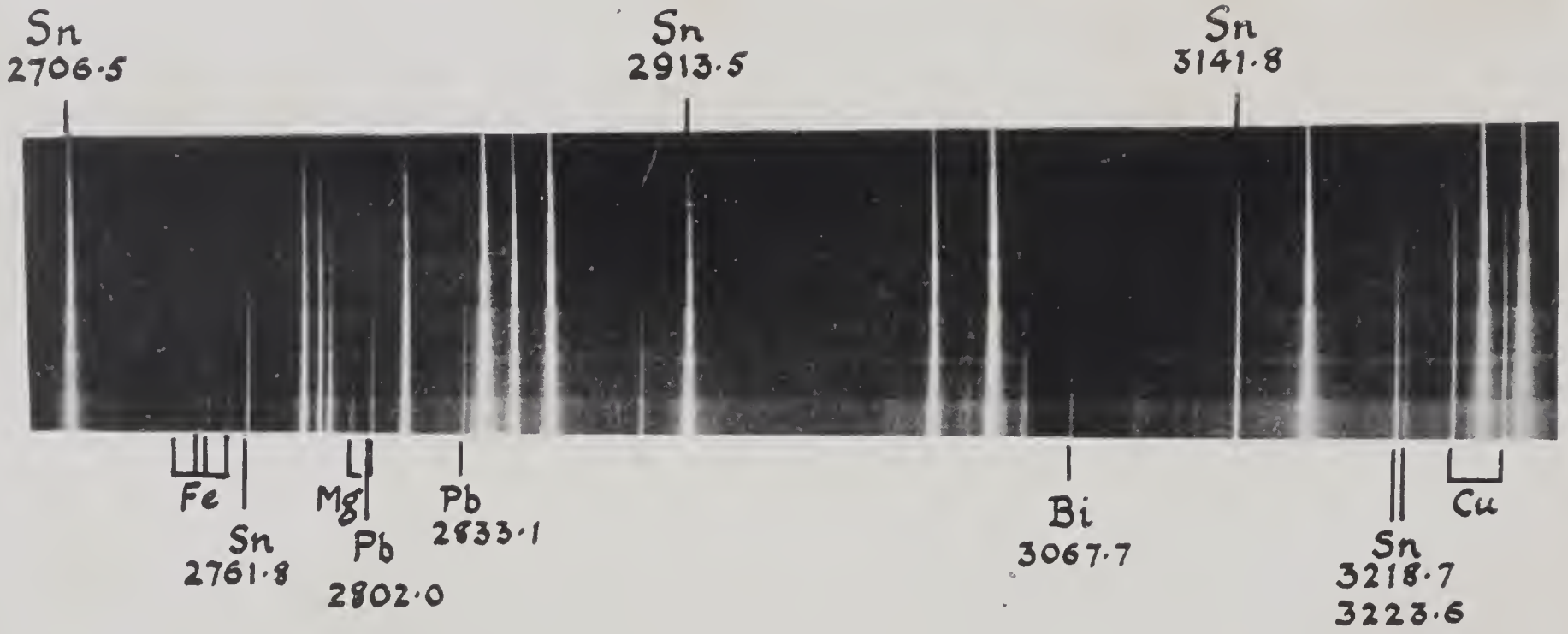




Faint lines due to the impurities lead, bismuth and copper are indicated. The dots indicate the spark lines of tin which decrease in intensity and recede towards the poles of the electrodes as the amount of added self-inductance increases. The 'pole' effect is shown by the stigmatic image on the slit, so that for intensity comparisons the spark is either used without a lens, as in (c) and (d) or focused within the optical system (see p. 4, Method 2) to give uniformity along the length of the line. The lines coupled together are the arc line 3330·594 Å *and the spark line* 3352·435 Å *used by Gerlach and Schweitzer to standardise the electrical conditions (see p. 13).*

PLATE II

STEPPED SPARK SPECTRA OF COMMERCIAL TIN



Spectra obtained from a condensed spark between metal electrodes, with 0.005 μF capacity and 0.03 mH added self-inductance in the secondary circuit.

(f) Alloys with Copper

Two alloys were prepared in the B.N.F.M.R.A. Laboratory by dilution of a sample containing 0·21 per cent copper (by chemical analysis) with electrolytically refined tin, melting and casting *in vacuo*. These were marked TCo1 and TCoo1, containing 0·01 per cent and 0·0015 per cent copper respectively.

Further work on the spectrographic determination of lead, bismuth, copper, silver, antimony, arsenic, iron, indium and nickel in tin, carried out in 1939, took the form of a detailed comparison between spectrographic and chemical analyses of a number of tin samples prepared by the International Tin Research and Development Council. In addition, independent chemical analyses (obtained by means of a D.C. arc between metal electrodes) carried out by Messrs Lucius Pitkin, Inc., New York, were made available.

From the data thus available, it was possible to compile analytical tables, based on the internal standard method and to make estimates of the limits of spectrographic detection. Some discretion was exercised in deciding which standards could be regarded as reliable, with a bias towards agreement between the independent spectrographic analyses.

2. Preparation of Samples for Analysis

Spark electrodes were prepared from 2 mm. thick sheet, both electrodes being about 1 cm. square and of the material under test. Samples of different shapes and sizes were rolled or hammered to give sheet of this thickness. The sparking area on each electrode was about 5 mm. × 2 mm., this being obtained by cutting off one corner. While care was taken to prepare electrodes of the same shape and size, no attempt at accurate standardisation was made. It should be noted, however, that for accurate analyses with the densitometer, particularly in the determination of volatile components, accurate shaping of the spark electrodes to a standard form is recommended. In this respect rod shaped electrodes of uniform diameter are advantageous.

Scribner[16] describes several methods for the preparation of electrodes for the spark. Formerly turnings of the metal were melted and cast in rod form in evacuated glass tubes, but subsequently turnings, millings or scrapings were compressed in a hydraulic pressing machine to give rods $\frac{1}{4}$ in. in diameter and $\frac{5}{16}$ in. in length. The sparking ends of the electrodes were turned flat with the edges slightly bevelled.

Observing that the vacuum-melting technique requires considerable care to avoid time-consuming failures, Scribner gives details of the necessary precautions to be taken.

The 'briquetting' technique, described above, is also of value in the analysis of small samples as these can be pressed into a thin layer on the end of a tin rod. The spark is then passed between the layers on two such rod electrodes.

3. The Spectra of Successive Exposures

(*A means of studying the variation of intensity with time.*)

At the commencement of the running of the spark discharge between tin electrodes, using the standard Hilger spark equipment and 0·19 mH added self-inductance, the sound made is different from that made after the discharge has become more steady (after 30 secs. or so). This effect seems to be more marked in the case of tin than with other metals, e.g. lead, aluminium, zinc.

The spectra of successive exposures of a continuously running spark were therefore photographed in order to study the effect on the spectrum of the different conditions of the discharge. It was observed that the first spectrum was stronger than the others and the spark line 3352·435 Å was stronger than the arc line 3330·594 Å while in the remaining spectra these two lines were of equal intensity.

At first, when the electrodes are cold the spark is more disruptive and spark-like in character, and when they have become heated more metal is vaporised into the spark gap, resulting in more arc-like conditions. Oxidation of the surface of the electrodes in the region of the discharge also occurs, but after the spark has been running for a short time a state of equilibrium is reached.

The question of the oxidation of lead and tin electrodes was studied in some detail by Töpelmann and Schuhknecht[9] who found that using the same electrodes for several successive spectrograms, the time of exposure had to be increased more and more to obtain the same density. For example, after sparking for 5 mins. it was found necessary to give 12 times the normal exposure in the case of lead electrodes and about 20 times with tin electrodes.

That the oxides produced by sparking are deposited more and more thickly on the electrodes is confirmed by their appearance under the microscope as a porous dross. Consequently, the spark passes with more difficulty. Töpelmann and Schuhknecht also observed that with the primary current strength maintained constant, the current strength in the discharge circuit decreased during the sparking of base metal electrodes. The smaller the current strength in the primary circuit the smaller was this 'sparking-off' effect.

Seith and Hofer[6] described a device for the removal of the 'vapour cloud' given by the spark and claimed that an extremely regular discharge was obtained in this way.

The relative intensities of the lead line 2614·178 Å and the tin line 2636·991 Å (both arc lines) were studied by Follett[12] who found that 'in every case a rapid fall in the ratio of the intensity of the lead line to that of the tin line occurred after switching on, but after 1½ minutes the ratio became constant. The course of the variation was not reproduced in the different experiments but in no case did systematic variation persist after 1½ minutes'. (Follett used 0·006 μF capacity and 0·25 mH added self-inductance.)

With high inductance in the spark circuit Scribner[16] observed that a short period was required before equilibrium was reached. Nevertheless he used no prespark period, as a loss in sensitivity in determining zinc resulted from the use of a prespark period, probably as a result of more rapid volatilisation during the early stages of sparking

Further tests were made, in the B.N.F.M.R.A. laboratory, of successive exposures of the spark with only 0·03 mH added self-inductance. A marked increase in regularity was observed as compared with the use of 0·19 mH or 0·25 mH and the value 0·03 mH was therefore adopted for the standardised method.

4. Prespark Period

A short presparking period has generally been regarded as desirable, partly as a means of removing any slight surface contamination of the electrodes and partly to avoid any initial instability of the discharge. The practice of presparking until constant emission is attained, as formerly followed by German spectroscopists, is not recommended. Scribner[16] used no prespark period.

5. Standardised Spark Technique

The following analytical tables (Tables III–XI) apply to spectra photographed under the following conditions:

Transformer: $\frac{1}{4}$ KVA high reactance transformer giving 15,000 v. open-circuit secondary voltage.

Capacity: 0·006 μF.

Added Self-Inductance: 0·03 mH.

Spark Gap: 3 mm.

Spectrograph slit irradiation: the spark was placed 20 cm. from the slit of the medium-size spectrograph and no condensing lens used.

Slit width: 0·02 mm.

Photographic plate: Ilford Thin Film Half-Tone.

Prespark/Exposure time: 20 secs./1 min.

Development: was continued until the group of tin lines in the region of 2100 Å was clearly visible on the developed plate. (This would be equivalent to $3\frac{1}{2}$ mins. in I.D.2 developer, with simple dish-rocking.)

6. Analytical Tables

The notation in the following tables conforms with the usual conventions, $<$, $=$ and $>$ indicating that the impurity line in question is respectively weaker than, equal in intensity to, or stronger than the tin line used as the internal standard; 'bv' indicates that the line is barely visible on viewing the photographic plate with a lens.

The wavelengths quoted in these and following tables, and in the text, are taken from the Massachusetts Institute of Technology Wavelength Tables.[31]

TABLE III.—ALUMINIUM

Al%	3082·155 Al	3092·713 Al
0·001	bv	—
0·0026	—	$<$
0·0035	$<$	$=$ 3223·574 Sn
0·005	$=$ 3223·574 Sn	$>$
0·01	$>$	$<$
0·02	$<$	$=$ 3218·684 Sn
0·04	$=$ 3218·684 Sn	$>$
0·06	$>$	$=$ 3141·809 Sn
0·1	$<$ 3141·809 Sn	$>$

TABLE IV.—ANTIMONY

Sb%	2311·469 Sb	2528·535 Sb
0·008	bv	bv
0·01	—	$<$
0·05	$<$	$=$ 2636·991 Sn
0·07	$=$ 2357·886 Sn	$>$ $<$ 2433·477
0·1	$>$	$=$ Sn

TABLE V.—ARSENIC.

As %	2349·84 As
0·01	bv
0·05	< } 2357·886 Sn
0·09	= }

TABLE VI.—BISMUTH

Bi%	3067·716 Bi	
0·0003	bv	
0·001	<	
0·006	= } 3223·574 Sn	
0·01	>	
0·025	< } 3218·684 Sn	<
0·05	= }	= } 2761·776 Sn
		>

TABLE VII.—CADMIUM

Cd%	2265·017 Cd*	2288·018 Cd	3466·201 Cd
0·001	bv	= } 2357·886 Sn	bv
0·003	—	>	—
0·005	<	= } 2282·236 Sn	—
0·006	= } 2282·236 Sn	>	—
0·01	>	—	<
0·03	= } 2267·190 Sn	—	= } 3223·574 Sn
0·05	>	—	>
0·1	< 2268·910 Sn	< 2286·680 Sn	< 3655·778 Sn

* This line is unsuitable for quantitative measurements if the arsenic line 2288·12 Å is also present. If this is the case, another arsenic line, 2349·84 Å, will probably also be present for confirmation.

TABLE VIII.—COPPER

Cu%	3247·540 Cu		3273·962 Cu
0·0005	bv		—
0·001	<		—
0·002	= } 3223·574 Sn		<
0·004	>	<	= } 3223·574 Sn
0·015		= } 3218·684 Sn	<
0·03	<	>	= } 3218·684 Sn
0·04	= } 3141·809 Sn		>

TABLE IX.—LEAD

Pb%	2833·069 Pb		3639·580 Pb	3683·471 Pb
0·004	n.d.*		n.d.	bv
0·006	bv		bv	—
0·01	—		—	<
0·02	—		<	= } 3223·574 Sn
0·05	—		= } 3223·574 Sn	>
0·1	< } 2761·776 Sn		>	—
0·23	=	<	—	—
0·3	>	= } 3218·684 Sn	—	<
0·5		>	—	= } 3655·778 Sn

* Not detected.

Table X.—Silver

Ag%	3382·891 Ag
0·0003 0·001 0·002 0·004 0·008 0·01	 = > } 3223·574 Sn bv < = > } 3218·684 Sn

Table XI.—Zinc

Zn%	2138·56 Zn	3302·588 Zn
0·001	bv	—
0·003	<	bv
0·005	= } 2140·08 Sn	—
0·01	>	< } 3223·574 Sn
0·02	—	=
0·05	—	< } 3218·684 Sn
0·1	—	=

Iron, Indium and Nickel: Suitable internal standard tin lines have not been found for the determination of these elements.

7. Limits of Detection

The estimated limits of spectrographic detection of the above elements in tin, using the spark method described, are given below:

Table XII

Element	Limit of Detection
Aluminium	Less than 0·001%
Antimony	0·008%
Arsenic	0·01%
Bismuth	0·0003%
Cadmium	Less than 0·001% (probably 0·0005%)
Copper	0·0005%
Indium	0·0005%
Iron	0·001%
Lead	0·004%
Nickel	0·001%
Silver	0·0003%
Zinc	0·001%

APPENDIX

Laboratory Purification of Tin by Electrolytic Refining

Experiments were made in the hope of obtaining spectrographically pure tin for use in the preparation of standard alloys containing very small quantities of the alloying constituents. The purest sample of tin available commercially at the time the experiments were made was 'Chempur' tin, the spectrum of which showed faint lines due to lead, bismuth, copper and iron as impurities.

Since the purity of the electrolyte determines the purity of the deposit, the following experimental conditions were finally adopted. A glass tank 10 × 6 × 6 in. was filled with an electrolyte of the following composition (all the materials having been checked spectrographically for purity):

Distilled water	3,000 ml.
Conc. hydrochloric acid (A.R. quality)	500 ml.
Conc. sulphuric acid (A.R. quality)	10 ml.
Ammonium chloride	25 gm.

Ammonium chloride was added to improve the deposit and to diminish the tendency to short-circuiting by the 'streamers' from the cathode.

Anodes of tin 5 in. long and 1 × $\frac{5}{8}$ in. in section were suspended at each end of the tank and immersed to a depth of $4\frac{1}{2}$ in. Three pure carbon cathodes $\frac{3}{8}$ in. diameter were suspended in the centre of the tank, symmetrically disposed with regard to the anodes. Glass dishes 2 in. diameter and $1\frac{1}{4}$ in. deep were placed under the anodes to collect the sludge. A current of 0·5 amp., at 0·6 volt, was passed until a small adherent deposit of tin had formed on the cathode, after which the current was raised to 1·2 amps. This gave needle-like crystals which were readily detached from the carbon rods. After washing with distilled water the crystals were melted in a graphite crucible and allowed to solidify.

A supply of this refined tin was kindly analysed by Messrs Capper Pass & Sons Ltd., and the results given below were obtained by careful analysis of a large sample. For comparison, the combined chemical and spectrographic analysis of the sample of tin before refining are also given:

Analysis of Pure Tin Samples

	Before refining (%)	After refining (%)
Lead	0·008	0·0026
Antimony	0·003	<0·001
Bismuth	0·003	0·0004
Copper	0·0005	0·0006
Iron	0·002 (estimated)	0·0003

ANALYSIS OF TIN-LEAD SOLDERS

1. Standard Alloys

Attempts were first made to prepare solder standards by melting, in evacuated Pyrex tubes, accurately weighed quantities of the component metals, but these proved unsuccessful.

(R. G. Ernst, of the United States Metals Refining Co., New Jersey, however, reported, in a private communication, the successful preparation of synthetic standards for the determination of zinc and bismuth in solders, by melting the constituents together in a glass tube under hydrogen. Whether this technique would give reliable standards for aluminium does not appear to have been investigated, this element giving the most difficulty as regards uniform distribution in the solidified alloy.)

Graded series of alloys of solder with aluminium, cadmium and zinc were kindly supplied by Mr J. Cartland of Messrs Fry's Metal Foundries Ltd., London. Alloys with bismuth were prepared in the B.N.F.M.R.A. laboratory. In view of the difficulty in obtaining satisfactory chemical checks on the composition of these alloys, synthetic solder residues were prepared, as ultimate standards of reference, by mixing solutions of the various components in the appropriate proportions and evaporating to dryness. Residues of the standard alloys, obtained by dissolving and evaporating, were then compared with the synthetic residues by means of graphite arc spectra.

2. Residue Method

The component metals were dissolved in appropriate acids and accurately measured quantities of the solutions were added together and taken to dryness with hydrochloric acid. By suitable dilutions of the solutions of the impurity metals, it was possible to produce a graded series of synthetic mixtures of accurately known composition. The residues were thoroughly ground and mixed before making the spectrographic tests, and since these residues were somewhat hygroscopic, precautions were taken to preserve them in a dry atmosphere until the completion of the tests.

Two series were prepared; in the first, the principal components were tin and lead in equal proportions, while in the second series, representing antimonial solders, the principal components were 50 per cent tin, 47·2 per cent lead and 2·8 per cent antimony. In each series, aluminium, bismuth, cadmium and zinc were added in the following proportions: 0·1, 0·05, 0·025, 0·01, 0·005, and 0·001 per cent respectively. A further sample was prepared from the pure tin and lead with no admixtures.

Spectrographic analyses of the lead and tin were made with the results shown in Table XIII. The other metals used were of the highest purity available.

Table XIII

Analysis of the Tin and Lead used in the Preparation of the Synthetic Residues

	Lead*	Tin†
Aluminium	not detected	not detected
Bismuth	0·0004%	0·002%
Cadmium	Less than 0·0001%	not detected
Copper	0·001%	0·003%
Zinc	not detected	not detected

* See No. 9 of 'Collected Papers.' (Ref. [28], pp. 110–115.)

† Analysed by means of the tables in Section I(6) of this booklet.

Table XIV gives the compositions of the synthetic residues corrected on the basis of the above analysis of the tin and lead used in their preparation.

The range of composition of the metallic alloys used in this work are indicated in Table XV below.

Table XIV.—Compositions of the Synthetic Residues

Tin-Lead (A series) and *Tin-Lead-Antimony* (B series)

Nos.	% Aluminium	% Bismuth	% Cadmium	% Zinc
A1, B1	0·1	0·1	0·1	0·1
A2, B2	0·05	0·05	0·05	0·05
A3, B3	0·025	0·025	0·025	0·025
A4, B4	0·01	0·011	0·01	0·01
A5, B5	0·005	0·0062	0·005	0·005
A6, B6	0·001	0·0022	0·001	0·001
A7, B7	—	0·0012	—	—

Table XV.—Compositions of the Standard Alloys

Element Studied	Percentage Range	% Sn	% Pb	% Sb
Aluminium	0·001–0·05	50·0	47·2	2·8
Bismuth	0·0012–0·1	45·0	52·5	2·5
	0·0013–0·1	50·0	50·0	—
Cadmium	0·001–0·05	50·0	47·2	2·8
Zinc	0·001–0·05	50·0	47·2	2·8

Table XVI gives the compositions of the chemically analysed samples used as standards with respect to copper.

Table XVI.—Standards for Copper

Alloy No.	% Tin	% Antimony	% Copper
37	27·80	1·58	0·10
38	44·34	trace	0·093
39	39·95	2·01	0·09
40	43·8	2·0	0·05
41	31·64	trace	0·02
42	60·17	0·24	0 01
43	44·35	trace	0 009
44	59·79	trace	0 007

3. Comparison of Synthetic Residues with Residues from Alloys to be used as Metallic Standards

Preliminary tests indicated that, when using a 5-amp. graphite arc for the analysis of solder residues, greater regularity in the spectra resulted from making the sample the positive electrode. Increasing the size of the sample led to an increase in the densities of the lines and continuous background in the spectrum.

Approximately equal quantities of the residues, sufficient to fill a shallow cavity in the lower electrode were used in each case, so that the conditions were maintained constant for synthetic residues and residues from alloys alike. The spectra were photographed with a medium size spectrograph (0·007 mm. slit width) using Ilford Special Lantern plates and giving an exposure of 1 minute (timed from the moment of striking the arc).

To obviate any possible disturbing effects due to the presence of antimony, comparison was made between residues of similar composition, i.e. synthetic residues A 1–7 for the analysis of residues from non-antimonial solders and synthetic residues B 1–7 for residues from antimonial solders.

For all the impurities studied except aluminium the residues gave spectra showing a systematic increase in the intensities of the impurity lines with increasing percentage content, thus enabling the contents of the alloys to be used as metallic standards to be ascertained by direct comparison of the spectra. Within the limits of visual observation, the compositions aimed at in preparing the alloys were confirmed and these alloys were then used for the compilation of analytical tables based on the internal standard method.

Irregularities were observed, however, in the case of the samples containing aluminium. Variations in intensity of the aluminium lines were observed in duplicate spectra and satisfactory correlation was not shown between intensity and percentage content. This is probably due to the volatility of aluminium chloride and possibly, in some measure, to formation of non-conducting alumina.

4. Standardised Spark Techniques

In view of the similarity between the spark spectra of tin and tin-lead solder, the standardised conditions of excitation and photography used for the analysis of tin were adopted for the determination of impurities in solder. The spark electrodes were in the form of rods, approximately 1·5 cm. long and 5 × 5 mm. cross-section, roughly pointed to an angle of about 70°.

In the laboratory of Fry's Metal Foundries Ltd., rod samples, 8 mm. in diameter and 12 cm. long, are prepared and the sparking ends are turned on a lathe to give cylinders of 5 mm. diameter and about 5 mm. in length, with plane ends. Apart from the insertion of 0·13 mH self-inductance in the circuit, the same excitation and photographic conditions are used as in the B.N.F.M.R.A. laboratory.

The quantitative analysis of white-metal (anti-friction alloy, containing 83 per cent. tin, 11 per cent. antimony and 6 per cent. copper, with lead, arsenic, iron and zinc as impurities) is described by J. Gillis, J. Eeckhout and M. van Doorsalaer* (of the University of Ghent). A Feussner (controlled) spark between a lower electrode of the white-metal sample and an upper electrode

* *Anal. Chim. Acta*, 1947, **1**, (4), 209-217.

of graphite was used, both electrodes being 3·8 mm. in diameter, the sparking ends turned flat and slightly bevelled.

Secondary voltage (*open circuit*): 12,000 v.

Capacity: 1,800 cm. (0·002μF.)

Self-inductance: 800,000 cm. (0·8 mH)

Spark gap: 3 mm.

A sharp point was mounted about 1 cm. from the spark, electrically connected to one electrode, to improve the regularity of the discharge.

Prespark/Exposure time: 30/75 secs.

A 5-step sector, rotating at 125 r.p.m., was used to determine the 'efficiency' difference (log. exposure time ratio, i.e. the separation of the blackening curves for the analysis line and the internal standard tin line) for all the elements studied. The concentration-calibration curves gave the relation between this quantity and the logarithm of the percentage of the element relative to the tin content.

The results obtained were statistically examined.

A paper entitled 'Routine Spectrographic Analysis of Solders and Babbitts' was presented by G. W. Wiener and A. W. Danko, at the Second Annual Analytical Symposium, Pittsburgh Section, American Chemical Society. The authors describe a method for the analysis of various materials including tin-base solders and babbitts. It is claimed that tin in tin-lead solders can be determined over the range 20 to 70 per cent., with an accuracy of ± 2 per cent of the amount present. A spark is obtained between a carbon rod and the sample in the form of a disc 1·5 in. in diameter and 0·5 in. thick, using a Petrey spark stand. Two superimposed exposures are photographed in order to reduce effects due to segregation. (Seen in Abstract only, *Anal. Chem.*, 1947, **19**, (4), 285.)

5. Choice of Internal Standards

In view of the closer resemblance of solder spectra to tin spectra than to lead spectra, only tin lines have been used as internal standards in Tables XVII–XX. No differences were detected between the relative intensities of the fainter tin and lead lines, e.g. Sn 3218·684 Å and 3223·574 Å and Pb 3220·538 Å in the spectra of the various types of solder examined, although somewhat different proportions of tin and lead were present. The internal standard lines are accordingly suitable for intensity comparison. Some of the fainter lead lines which might otherwise have served as supplementary internal standards were found to be somewhat diffuse and therefore unsuitable.

On the other hand, in the spectrographic laboratory of Fry's Metal Foundries Ltd., use is made of both tin and lead lines as internal standards for the analysis of solders containing 50 per cent. tin, 2·5 per cent. antimony, remainder lead. The electrical conditions only differ from those used in the B.N.F.M.R.A. laboratory in the value of added self-inductance, viz. 0·13 mH (see Table XXI).

McClelland and Whalley[17] used the lead line 2628·263 Å as an internal standard line for measurements with the densitometer and lead lines are also given in the A.S.T.M. Tentative Standard Method.[21]

Kerckhoff[18] studied the determination of antimony in lead and solder (58–62 per cent lead). The effect of the tin was to give high results for the Sb contents of solders when determined by comparison with lead-antimony standards, using the line pair Pb 2332·426/Sb 2311·469. The calibration curve for the solder standards was parallel to that for the lead standards. This subject was studied further by Balz[19] who observed that the data for both lead and solder fitted the same calibration curve if the antimony content was calculated on the (Pb + Sb) content in each case.

6. Analytical Tables

(a) B.N.F.M.R.A.

TABLE XVII.—BISMUTH

Bi%	3067·716 Bi
0·001 0·004 0·01 0·025 0·05	<, =, > 2761·776
	<, =, > 3223·574 Sn
	<, > 3218·684 Sn (estimated equality at 0·04% Bi)

TABLE XVIII.—CADMIUM

Cd %	2265·017 Cd	2288·018 Cd*	Cd %	3466·201 Cd
0·001 0·005 0·01	<, =, > 2282·236 Sn	=, > 2357·886 Sn <, =, > 2282·236 Sn	0·001 0·005 0·01	— — bv
0·02	<, =, > 2266·04 Sn	2312·84 Cd	0·02 0·05	=, > 3223·574 Sn
0·05 0·1	— —	<, = 2282·236 Sn	0·1	—

* This line is unsuitable for quantitative measurements if the arsenic line 2288.12 Å is also present. If this is the case, another arsenic line, 2349.84 Å, will probably also be present for confirmation.

TABLE XIX.—COPPER

Cu %	3247·540 Cu	3273·962 Cu
0·007 0·009	=, > 3223·574 Sn	<, =, > 3223·574 Sn
0·02 0·03 0·05	<, =, > 3218·684 Sn	<, =, > 3218·684 Sn
0·1	—	<, = 3141·809 Sn

TABLE XX.—ZINC

Zn %	2138·56 Zn*	3302·588 Zn	3345·020 Zn
0·001	by	—	—
0·002	= 2140·08 Sn	—	>
0·005	>	<	= 3223·574 Sn
0·01	—	= 3223·574 Sn	<
0·03	3072·062 Zn	> < 3218·684 Sn	= 3218·684 Sn
0·05	< 3223·574 Sn	> (equality estimated at 0·04% Zn)	>
0·1	=		—

* Care should be taken to distinguish between this line and the antimony line 2139.76Å in the spectra of antimonial solders.

DETERMINATION OF ALUMINIUM. For small quantities of this element the aluminium lines 3082.155Å and 3092.713Å may be compared with the tin lines 3223.574 and 3218.684Å and, for higher quantities, 3141.809Å. (Cf. Table III.)

(b) Fry's Metal Foundries Ltd.

TABLE XXI

%	Index Points		Index Points	
	Arsenic		*Nickel*	
0·001	As 2349·84	bv	Ni 3414·765	= Sn 3412·8
0·003		< Pb 2253·95	Ni 3101·554	= Pb 3118·19
0·01		= Pb 2253·95	Ni 3101·554	= Sn 3223·574
0·03		= Sn 2357·886	Ni 3134·108	= Sn 3223·574
0·1		= Sn 2266·04	Ni 3101·554	= Sn 3218·684
	Bismuth		*Silver*	
0·001	Bi 3067·716	= Sn 3223·574	Ag 3382·891	= Sn 3218·684
0·003		= Pb 3220·538	Ag 2437·791	= Pb 2717·37
0·01		= Sn 3218·684		= Pb 2253·95
0·03	Bi 2897·975	= Pb 2657·106		= Sn 2433·477
0·1		= Sn 3218·684		= Sn 2266·04
	Cadmium		*Zinc*	
0·001	Cd 2265·017	= Pb 2253·95		—
0·003		= Sn 2251·15	Zn 3345·020	bv
0·01		= Sn 2266·04	Zn 3302·588	= Pb 3232·353
0·03	Cd 3403·653	= Sn 3223·574		= Pb 3220·538
0·1		= Sn 3218·684		= Sn 3141·809
	Iron			
0·001	Fe 2719·025	bv		
0·003		= Pb 2717·37		
0·01	Fe 2382·039	= Pb 2253·95		
0·03		= Sn 2266·04		
0·1		= Sn 2368·226		

McClelland and Whalley[17] used the spark between metal electrodes (added inductance 0·125 mH) for the analysis of solders. Aluminium, zinc, silver, bismuth, arsenic and iron were estimated visually, but for copper and cadmium up to 2 per cent and antimony up to 1·5 per cent a densitometer was used. In the latter case the 'variant exposure' method of analysis was used, in which, after a prespark period of 10 secs., exposure times of 10, 20, 14 and 16 secs. were given.

Variant Exposure Method (H. K. Whalley)

A linear relation was found to exist between d_1/d_2 and d_2 where d_1 and d_2 are the densitometer readings for the lines due to the impurity and basis metal, respectively (i.e. the analysis and internal standard lines). Thus by giving several exposures of different duration, a series of straight lines is obtained, corresponding to different percentage contents. Alternatively, a series of curves may be obtained by plotting d_1 against d_2. From these curves the value of the ratio corresponding to an arbitrary or pre-determined value of d_2 may be read off and the ratio values thus obtained are then used in the preparation of the concentration-calibration curve.

(This method provides some compensation for variations in the overall densities of the spectra. On general grounds, however, it is preferable to improve the source of excitation to increase the reproducibility of the spectra.)

7. Effect of Antimony as a Third Alloy Component

Using methods of visual examination for the determination of bismuth in solders, the presence of 2·5 to 2·8 per cent antimony appeared to have no effect on the relative intensities of bismuth and internal standard tin lines as compared with the spectra of non-antimonial solders. In other words, direct comparison may be made between antimony-free and antimonial solders so far as the determination of bismuth is concerned. Whether this also holds for the other impurities is a matter for further investigation. The tin and lead contents of the antimonial solders differ from those of the non-antimonial solders, but these differences are such that they are not detected by ordinary visual comparison of spectra.

With the use of the densitometer it is possible that a small shift in the concentration-calibration curve, due to the presence of antimony, may be detected, on account of the much higher accuracy attained by this method of analysis.

8. A.S.T.M. Tentative Standard Method

The earlier investigations led to the conclusion that while the residue method of analysis was useful to check the composition of alloys to be used as metallic standards, it was unsuitable for routine analyses. This was partly because of the time and manipulation involved but it was also admitted that a more detailed study of graphite arc methods for the analysis of residues was desirable.

Methods involving the use of solutions are out of the question as lead sulphate and chloride are insoluble and tin is precipitated in nitric acid as metastannic acid.

Ruehle and Jaycox[20] observing that solder bars are frequently variable in composition from point to point adopted a powder residue technique which has given satisfactory results for some years.

Samples are dissolved in 15 per cent nitric acid, taken to dryness, baked and ground to a fine powder in an agate mortar. The powder is then thoroughly mixed with an equal weight of purified carbon dust containing 20 per cent by weight of pure ammonium nitrate. The analysis is then made by means of a graphite arc, taking 9 amps., the sample being placed in a hole $\frac{1}{8}$ in. deep in the lower, positive, electrode.

For the purpose of plate calibration an extra exposure is made of the highest standard through a stepped sector.

In 1943 this method was issued as a tentative standard method by the American Society for Testing Materials.[21] The method is written from the standpoint of lead-tin solders only, but it is stated that it is also applicable to the analysis of tin-base die-casting alloys, composed of tin, antimony and copper, and of bronzes. Full directions are given for the preparation of a range of standards and of the samples for analysis. When samples are tested to specification impurity limits, visual comparison of the spectra is often sufficient to determine that the sample is well within the specification. In doubtful cases, or where accurate analyses are required, the use of the densitometer is recommended, line densities being converted to relative intensities by means of the calibration pattern.

No internal standard is given for the determination of aluminium by means of the lines 3082·155 and 3092·713Å. The lead line 2657·106Å serves as an internal standard for the determination of antimony, arsenic, bismuth, iron and nickel and Pb 3220·538Å for zinc and copper.

BIBLIOGRAPHY

Papers published up to 1935

[1] W. F. Meggers, C. C. Kiess and F. J. Stimson. 'Practical Spectrographic Analysis. *U.S. Bur. Standards Sci. Papers*, 1922–23, **18**, No. 444, 235–255.

[2] T. Negresco. 'Recherches Expérimentales d'Analyse Spectrale Quantitative sur les Alliages Métalliques.' *Les Presses Universitaires de France*, Paris, 1927.

[3] W. Gerlach and E. Schweitzer. 'Die chemische Emissionsspektralanalyse.' I. L. Voss, Leipzig, 1929. (Authorised translation published by Adam Hilger Ltd.: 'Foundations and Methods of Chemical Analysis by the Emission Spectrum').

[4] G. Scheibe, C. F. Linström and O. Schnettler. 'A Method of Increasing the Accuracy of Quantitative Spectrographic Analysis and its Testing'. *Z. angew. Chem.*, 1931, **44**, 145–151.

[5] R. Breckpot. 'Quantitative Spectrum Analysis of Pure Metals.' *Natuurw. Tijdschr.*, 1934, **16**, 139–143.

[6] W. Seith and E. Hofer. 'Contributions to Quantitative Optical Spectrum Analysis.' *Z. Elektrochem.*, 1934, **40**, 313–322.

[7] H. Kringstad. 'Spectrographic Determination of Lead in Commercial Tin.' *Angew. Chem.*, 1935, **48**, 565–566.

Logarithmic Sector Method

[8] G. Scheibe and A. Neuhäusser. 'Rapid Determination of Alloying Constituents in Iron by Quantitative Emission Spectrum Analysis. *Z. angew. Chem.*, 1928, **41**, 1218–1222.

[9] H. Töpelmann and W. Schuhknecht. 'Quantitative Spectrographic Analysis of Alloys'. *Z. anal. Chem.*, 1931, **86**, 160–174.

[10] C. S. Hitchen. 'Quantitative Estimation of the Impurities in Tin by means of the Quartz Spectrograph.' *A.I.M.E. Tech. Publ.* No. 494, 1933, 20 pp. Abstract and discussion, *Trans. A.I.M.E.*, 1933, **104**, 353–359.

[11] J. W. Stewart. 'The Spectrographic Analysis of Tin.' *Proc. Amer. Soc. Test. Mat.*, 1939, **39**, 788–793, discussion, 794.

Analysis of Tin

[12] D. H. Follett. 'A Photometric Method Suitable for Spectrum Analysis.' *J. Sci. Inst.*, 1936, **13**, 221–228.

[13] R. Breckpot. 'Polarity Effects in the Spectrographic Analysis of Zinc and Tin.' *Natuurw. Tijdschr.*, 1936, **18**, 173–180.

[14] R. Breckpot. 'Quantitative Spectrographic Analysis of Lead, Tin and Cobalt.' *Ann. Soc. Sci. Bruxelles*, 1937, **57**, 129–140.

[15] R. Breckpot and J. Eeckhout. 'Spectrographic Analysis of Tin.' *Natuurw. Tijdschr.*, 1938, **20**, 92–95.

[16] B. F. Scribner. 'Spark Spectrographic Analysis of Commercial Tin.' *J. Res. Nat. Bur. Standards*, Feb. 1942, **28**, 165–190.

Analysis of Solder

[17] J. A. C. McClelland and H. K. Whalley. 'The Quantitative Analysis of Solder, Spelter, Magnesium and Aluminium Alloys.' *Spectrochim. Acta*, 1939, **1**, (1), 21–30.
[18] W. Kerckhoff. 'On the Influence of Third Alloying Components in Quantitative Spectrographic Analysis. Determination of Antimony in Lead and Solder.' *Metallwirtschaft*, 1939, **18** (38), 799.
[19] G. Balz. 'Determination of Antimony in Lead and Solder.' *Ibid.*, pp. 937–938.
[20] A. E. Ruehle and E. K. Jaycox. 'Some Observations on the Use of Powders in Spectrochemical Analysis.' *J. Opt. Soc. Amer.*, 1943, **33**, (2),109–112.
[21] 'Tentative Method of Spectrochemical Analysis of Tin Alloys for Minor Constituents and Impurities.' E51–43T. 1946 *Book of A.S.T.M. Methods of Chemical Analysis of Metals*, pp. 364–366.

Studies on Tin-Lead Spark Spectra

[22] F. de Boer. 'Influence of Composition on Spectrum Line Intensity in the Spark.' *Z. Elektrochem.*, 1940, **46** (10), 591–594.
[23] F. de Boer. 'Distribution of Intensity in Spectrum Lines Across the Spark Gap.' *Ibid.*, pp. 594–595.

Excitation Sources

[24] G. W. Kingsbury and J. A. C. McClelland. 'The Spectrographic Determination of Impurities in High Purity Zinc and Zinc Alloys for Die Casting by the Intermittent A.C. Arc Technique.' In 'Polarographic and Spectrographic Analysis of High Purity Zinc and Zinc Alloys for Die Casting.' H.M. Stationery Office, London, 1945, pp. 49–65. (See also B.S. 1225: 1945.)
[25] A. Walsh. 'A General-Purpose Source Unit for the Spectrographic Analysis of Metals and Alloys.' *Bulletin*, B.N.F.M.R.A., No. 201, March, 1946, pp. 60–80.
[26] M. F. Hasler and H. W. Dietert. 'A New Spectroscopic Source Unit.' *J. Opt. Soc. Amer* , 1943 **33**, (4), 218–228.
[27] C. G. Carlsson and R. Rynninger. 'Electrical Apparatus for Light Emission in Spectrum Analysis.' *Jernkontorets Annaler*, 1947, **131**, (1), 1–25.

Reference Books

[28] 'Collected Papers on Metallurgical Analysis by the Spectrograph.' (Edited by D. M. Smith.) British Non-Ferrous Metals Research Association, London, 1945.
Although this collection does not include any reference to the analysis of tin, the following papers are of interest from the point of view of general spectrographic technique:
(*a*) 'Recommendations for the Processing of Photographic Plates in Spectrographic Analysis.' (Report of the B.N.F.M.R.A. Photographic Panel.) Pp. 1–10.
(*b*) 'Some Aspects of the Quantitative Spectrographic Analysis of Aluminium and its Alloys.' (Contribution from the Laboratories of the British Aluminium Company Ltd.) Pp. 29–64.
(This paper deals in a comprehensive manner with the subject, the section on 'Photographic Aspects' being of particular interest in the present connection.)
(*c*) 'A Technique for the Spectrographic Analysis of Lead Alloys for Cable Sheathing.' (Report of the B.N.F.M.R.A. Lead Panel.) Pp. 94–99.
(Gives directions for the preparation of standard alloys by melting and casting *in vacuo* and includes a statistical test for ascertaining the analytical reproducibility of a given spectrographic method.)
[29] F. Twyman. 'The Spectrochemical Analysis of Metals and Alloys.' C. Griffin & Co. Ltd., London, 1941. (A second edition is in course of preparation.)
[30] W. R. Brode. 'Chemical Spectroscopy.' John Wiley & Sons, Inc. New York. (2nd Edition.) 1943.

Wavelength Tables

[31] G. R. Harrison. 'Wavelength Tables of 100,000 Spectrum Lines.' John Wiley & Sons, Inc., New York, 1939.

MK 25-11-58

820

MK 1-9-59

Ready

27/5/97

CHECKED
2008

VERIFIED
2013

SV2013